

A THERMODYNAMIC STUDY OF THE LIQUID Pb-Bi ALLOYS AT 823°K

By
Km VIJAYAKUMARI C DAS



DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST, 1975

A THERMODYNAMIC STUDY OF THE LIQUID Pb-Bi ALLOYS AT 823°K

A Thesis Submitted
in partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
Km VIJAYAKUMARI C DAS

to the

DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST, 1975

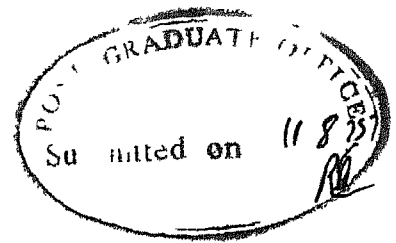


IMPUR
CENTRAL LIBRARY
Acc. No. 45522.

31 JAN 1976

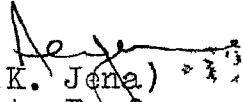
11
649
D26t


ME - 1975 - M - DAS - THE



CERTIFICATE

This is to certify that the work 'A THERMODYNAMIC STUDY OF THE LIQUID Pb-Bi ALLOYS AT 823°K' has been carried out by Kumari Vijayakumari C. Das under my supervision and that it has not been submitted elsewhere for a degree.


(A.K. Jena)
Associate Professor
Dept. of Metallurgical Engineering
Indian Institute of Technology
Kanpur.

POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
Master of Technology (M. Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur
Dated. 23.8.75 

ACKNOWLEDGEMENTS

It is my pleasure to express my heartfelt thanks and earnest appreciation of Professor A.K. Jena without whose painstaking guidance and perpetual encouragement this work could not have been completed. Thanks are also due to Professor A. Ghosh, Professor M.L. Vaidya, Professor T.R. Ramachandran and Professor M.N. Shetty for helping us with materials

Messers J.N. Sharma and C.M. Sharma of central glass blowing shop, Mr. V.P. Gupta of Met. Engg. workshop and Mr. K.P. Mukherjee of physical metallurgy lab. helped us to fabricate the apparatus. Their co-operation is gratefully acknowledged I appreciate the co-operation of Mr. R.C. Agarwala in this joint project.

Last but not least I thank Mr. R.N. Srivastava for typing the thesis.

CONTENTS

CHAPTER		Page
I	INTRODUCTION	1
II	REVIEW OF LITERATURE	2
	2.1 Various Methods	2
	2.2 The E.M.F. Technique	4
	Electrolyte	6
	Purification of electrolyte	7
	Electrodes	9
	E.m.f. measurements	10
	Temperature measurements	11
	2.3 The Pb-Bi System	11
III	EQUIPMENT AND PROCEDURE	14
	3.1 Furnace and Temperature Control	14
	3.2 Design and Fabrication of Cell	15
	3.3 Purification of Gas	16
	3.4 Vacuum System	17
	3.5 Temperature and E.M.F. Measuring Unit	17
	3.6 Experimental Procedure	18
	3.6.1 Cleaning of the apparatus	18
	3.6.2 Preparation of electrolyte	18
	3.6.3 Preparation of electrodes	21
	3.6.4 Measurement of e.m.f.	22

CHAPTER		Page
IV	RESULTS	24
	4.1 The Partial Molar Free Energy and the Activity of Lead	24
	4.2 Partial Molar Free Energies of the Components in the Pb-Bi Alloy	25
	4.3 Integral Molar Properties	27
V	DISCUSSIONS	36
	5.1 Sources of Errors	36
	Side reactions	36
	Stray e.m.f.	38
	Cell reversibility	38
	Ionic conduction	39
	5.2 Comparison With Other Data	39
	5.3 Internal Consistency of the Results	40
	5.4 The Bonding in the Pb-Bi Alloys	40
VI	SUMMARY AND CONCLUSIONS	44
	REFERENCES	45

CHAPTER - I

INTRODUCTION

In recent years molten metal systems have been examined in the light of various kinds of experimentally measured quantities. All these methods contribute in varying degrees to the structural and thermodynamic properties. The thermodynamic properties of liquid alloys are much useful in case of extraction, refining, alloy making, theory of alloys. Especially low melting alloys like Pb-Bi are needed in the reactors for heat transfer purposes and other nuclear engineering applications.

In this context the low melting Pb-Bi alloys are of importance. The melting point of lead is 327°C and that of bismuth is 271°C . These two metals form a eutectic system with a eutectic temperature of only 125°C . The lead is more electropositive than bismuth in the electrochemical series. In ~~this~~ investigation the thermodynamic properties of this system has been measured at 823°K by the e.m.f. technique and the structural characteristics of these alloys have been discussed.

CHAPTER - II

REVIEW OF LITERATURE

2.1 Various Methods^(1,2)

In one of the methods the vapour pressure of one of the components of the alloy is measured as a function of composition. Many experimental methods have been recently developed for this purpose. It is possible to calculate various thermodynamic properties from this data. Though the results of the evaporation studies have yielded much useful thermodynamic information it is not sufficiently reproducible to provide much information concerning the structure and nature of the bonding in the surfaces of solid materials.

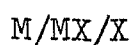
The calorimetric technique measures the changes in the enthalpy of heat content of substance, associated with changes in temperature, changes of states such as melting and boiling, changes of chemical combination such as reactions and alloying, dissolution or changes of physical structure, annealing, recovery and grain growth etc. But it is not possible to measure heats of reaction at low temperatures directly. The energy change of interest may have to be obtained as the small difference between two large quantities with the consequent need for high precision

in the measurement. These methods measure the total energy difference between two states and kinetic studies are therefore tedious.

The well-known three electrochemical techniques are the ones which use the aqueous, molten and solid electrolytes for the determination of the thermodynamic quantities. Because of the evaporation of electrolyte at working temperatures the scope of the former one is limited. For high temperatures solid electrolytes are most convenient. But many systems can not be investigated with solid electrolyte particularly at low temperatures as the electrolyte must have a minimum conductivity of $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ which is only achieved at elevated temperatures. Moreover its use is limited because of the appearance of the electronic conductivity under highly reducing conditions. The molten electrolyte technique has got the advantage that the required conducting ion may be brought into the neutral fused halides, oxides, acetates melts by dissolving small amounts of the salt or compound for the conducting ion in the suitable melt. By this technique the thermodynamic properties of binary, ternary, quaternary systems etc. intermetallic compounds, carbides, sulphides etc. can be studied.

2.2 The E.M.F. Technique

Theory: It is possible to obtain the changes in free energy of a reaction by measuring the e.m.f. of a suitable galvanic cell where the reaction is made to occur electrochemically⁽³⁾. Thus in the following chemical cell,



where MX is the electrolyte (an ionic conductor) and the electrodes M and X gives an e.m.f. This e.m.f. is related to the standard free energy of formation of MX by the expression

$$\Delta G_{MX}^{\circ} = -nEF$$

where all the components are in their standard states and n is the number of electrons transferred during the reaction, F is the Faraday constant and E is the e.m.f. . If one measures the e.m.f. as a function of temperature their enthalpy and entropy changes can also be estimated.

One of the most important information available by this technique is the activity of a component in a binary or a multicomponent system. The reversible cell of the following type can be constructed for this purpose

Pure metal (A)	Electrolyte containing ions of metal (A)	Solution of metals (A) and (B)
-------------------	--	--------------------------------------

If one gm-atom of metal is transferred from pure metal to an alloy the amount of work done is,

$$RT \ln a_A = - nEF$$

And a_A can be found out. To obtain reliable thermodynamic data one must however arrange to have well defined experimental conditions. So the following points should be kept in mind.

1. All exchange reactions between the alloy and the electrolyte must be absent.
2. Atmosphere surrounding the cell must not take part in the reaction.
3. Diffusion in the alloy must be fast to maintain a homogeneous alloy electrode.
4. Electrolyte must be purely ionic.
5. The electrodes and the electrolytes used must be pure.
6. Reversibility of the cell must be established beyond doubt.

Actually there is no single criterion which establishes the reversibility of an electrolytic cell. But if the following points are satisfied by any cell we can assume the cell to be reversible.

i) The e.m.f. values obtained on heating and cooling coincides within the limits of experimental errors.

ii) There should be no attack apart from a slight etch on the electrodes and there should not be any detectable change in their surface compositions.

iii) The potentials measured by a null method were in themselves **should** be reversible.

iv) The side reaction should not be present. If any such reaction is present corrected values should be taken⁽⁴⁾.

Electrolyte. A large number of investigations have been carried out using the fused salt electrolyte^(5-33,40-44). An eutectic mixture of AgCl + KCl was used by Ölander⁽⁵⁾. Pure fused $\text{Ag}_2(\text{NO}_3)_2$ and molten solution of AgCl was used by Watcher⁽⁶⁾. An eutectic mixture of KCl and LiCl and some amount of baser chlorides were used by a number of workers^(7,12,14,16,19,20-23,26-30,32,33). Molten equimolar mixture of KCl and NaCl with small amount of baser chlorides were used by Egan⁽²¹⁾, Pratt⁽⁸⁾ and Seigle⁽¹⁵⁾. Molten equimolar solutions of AgCl_2 and NaCl_2 ^{were} used by Hillert et al⁽¹⁰⁾. The mixture of KCl, NaCl, AlCl_3 ~~were~~ used by Wilder⁽¹¹⁾. Mixture of LiCl and RbCl, sodium and potassium acetates were used by Ölander⁽¹³⁾. Eutectic mixture of LiBr and RbBr^{was used} by Trunbore et al⁽²⁵⁾.

Purification of Electrolyte Metallic sodium was added to the electrolyte by Kleppa⁽¹²⁾ to reduce oxidation of metal due to the traces of H_2O present. Olander⁽¹³⁾ added $CdCl_2$ and Cadmium acetate to the electrolyte. Oriani⁽¹¹⁾ added $RbCl$. Seigle⁽¹⁵⁾ had added .2 mole pct. of $FeCl_2$ and .5 mole pct. of NH_4Cl . Fused KOH was added to neutralise the Hydrogen ions which might have formed from hydrolysis of moisture in the salt by Chipman and Elliott⁽¹⁹⁾ and Taylor⁽²⁰⁾. NH_4Cl was added by Melgren⁽³²⁾ for preventing hydrolysis. For the same reason Trunbore et al⁽²⁵⁾ added NH_4Br .

Wagner⁽³⁴⁾ heated the mixture of $LiCl$, KCl and $CdCl_2$ with NH_4Cl at $350^\circ C$ until all NH_4Cl was vapourised. He also melted $LiCl$, KCl , $SnCl_2$ under stream of purified HCl and subsequently in purified N_2 . Rosenthal et al⁽³¹⁾ dehydrated the electrolyte under vacuum at $150^\circ C$ before placing it in the shell and the final dehydration was affected by the application of moderate heat at 10^{-3} mm of Hg. Elliott and Chipman⁽¹⁹⁾ melted KCl , $LiCl$ at $400^\circ C$, added fused KOH and small amount of Cadmium pellets and then the temperature was raised to $500^\circ C$. After one hour the temperature was lowered to $400^\circ C$. The electrolyte was finally filtered through pyrex glass wool. Hillert et al⁽¹⁰⁾ purified the electrolyte by electrolysis at $350^\circ C$ for 24-36 hours with 2 V between graphite electrodes under an

atmosphere of dried argon. Latinen et al⁽³⁵⁾ evacuated the mixture of LiCl, KCl at .15 to .2 mm Hg for 6 hours. Then ground it to a fine powder by ball mill. Evacuated this for 3 days and raised the temperature to 300°C in 8 hours. The temperature was again raised to 500°C, HCl was passed, the cell was evacuated and it was filled with argon. The cell was again evacuated and filled with argon. Gardner et al⁽³⁶⁾ ground the fresh chlorides to ASTM 30 mesh, heated to 100°C under vacuum and then raised the temperature to 500°C. These chlorides were mixed in a dry box and transferred to the cell. Salomons et al⁽³⁷⁾ carried out similar process as Gardner et al⁽³⁶⁾ and in addition to it they treated the mixture with HCl and evacuated for a long time. Oriani⁽⁷⁾ prepared equimolar mixture of KCl, LiCl and some amount of AgCl and CuCl in separate container by holding at 500°C in contact with pure Ag or Cu wire for atleast 3 days under vacuum of about 1 μ Hg. Meanwhile the cell itself was prepared by holding it under the same vacuum at a temperature above the melting point of the alloy. The electrolyte was forced in to the cell by pure helium. Pratt⁽⁸⁾ dehydrated the equimolar mixture of KCl, NaCl by prolonged heating under vacuum. The mixture of alkali halides with some NH₄Cl was loaded in to a recrystallized alumina crucible and placed in a continuously evacuated and heated silica chamber. The

temperature was progressively raised from 200°C to 660°C in 7 days. .1 mole pct. of AgCl which had been similarly dehydrated at 200°C was added to the molten salt. Kleppa⁽¹²⁾ melted LiCl and KCl in a cell and degassed by heating for sometime at $600\text{--}650^{\circ}\text{C}$. Metallic sodium was treated with it in molten state. Oriani⁽¹⁴⁾ took KCl and LiCl in an auxiliary container and held at 400°C in contact with pure Cu wire under constant evacuation for 4 days. Some amount of RbCl was added to attain lower temperatures without freezing of the electrolyte. Melgren⁽³²⁾ dehydrated KCl and LiCl separately at $230\text{--}250^{\circ}\text{C}$ in 24 hours. NH_4Cl was added which decomposed to HCl and NH_3 . The salt mixture was melted in an argon atmosphere and heated slowly to 600°C .

Electrodes: The solid electrodes were used by a number of people^(5-10,14,15,25,28,32). The electrodes in the liquid form were used by a number of workers^(11-13,16-19,21-24,26,29-31,33).

Olander⁽⁵⁾ prepared alloys from .999 Au and .99975 Ag. Electrodes used by Oriani^(7,14) were 99.99 pct. pure. Pratt⁽⁸⁾ used 99.99 pct. pure Ag and 99.95 pct. Pd. Wilder⁽¹¹⁾ used 99.999 pct components. Kleppa⁽¹²⁾ used Bi containing .03 pct. Au and Tl containing .007 pct. Au. Olander⁽¹³⁾ used components pure up to .9999. Kleppa⁽¹⁸⁾

used Sn containing less than .04 pct. Pb, less than .01 pct. Fe, less than .004 pct. Cu and Sb, less than .002 pct. Bi. Au used was 99.9 pct. pure. Chipman and Elliott⁽¹⁹⁾ used Pb in amounts equal to .001 of atom fraction of Sb in case of Cd-Sb alloys. Strickler and Seltz⁽²²⁾ used metals purified electrolytically, the Pb being plated from Bett's⁽³⁸⁾ bath and Bi by a method described by Swift⁽³⁹⁾. Seltz and Dunkerley⁽²³⁾ used chemically pure Sn containing less than .01 pct. of impurities. Trunbore et al⁽²⁵⁾ used samples free of metallic impurities within .02 to .05 pct. Seltz et al⁽²⁶⁾ used commercially pure Cd containing less than .005 pct. impurities. Rosenthal⁽³¹⁾ used Pb 99.9995 pct. pure and Zn 99.999 pct.

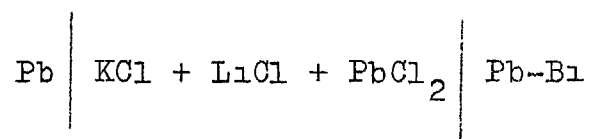
E.M.F. Measurements The lead wires used for measuring the e.m.f. was Ag welded with Cu wires^(5,8). A number of investigators used W lead wires^(7,12,16-20,23,24,32,33) Hillert et al⁽¹⁰⁾ used Al protected by quartz tubes. Wilder⁽¹¹⁾ and Egan⁽²¹⁾ used Ta lead wires. Oriani⁽²⁸⁾ used Pt suspension wires which were Ag soldered with W wires. Hildebrand and Sharma⁽³⁰⁾ soldered W wires with heavy Au wires

Reproducibility of measurements have been reported to be $\pm .01 \text{ mV}^{(17,10)}$, $\pm 0.02 \text{ mV}^{(26)}$, $\pm 0.05 \text{ mV}^{(19,30)}$, $\pm .1 \text{ mV}^{(5,6,9,17,33)}$, $\pm 0.2 \text{ mV}^{(17)}$, $\pm 0.3 \text{ mV}^{(24)}$ and $\pm .5 \text{ mV}^{(12)}$.

Temperature Measurements For temperature measurements chromel-alumel^(5,6,11,17,19,21,30), iron constantan⁽²²⁾ and Pt-Pt, Rh (10 pct.)^(7,31) thermocouple have been used. The temperature ranges used for the e.m.f. measurements are shown in Table 2.1.

2.3 The Pb-Bi System

The Pb-Bi alloys can be used to form a cell of the type given below.



The difference in the standard free energy of formation of chlorides of the components in the binary system investigated by the e.m.f. techniques are shown in Table 2.1.

At 500°C / ΔG° of formation of PbCl_2 from its components⁽³⁾ is -58 Kcal/mole and for BiCl_3 , -38 Kcal/mole. Since the difference of ΔG° is 20 Kcal/mole which is quite appreciable amount, this cell is feasible (Table 2.1)

Table 2.1
Temperature Ranges and $\Delta(\Delta G^\circ)$ for Chlorides

System	Components whose activity is measured	Range of temperature °K	$\Delta(\Delta G^\circ)$ Kcal for chlorides	Reference
Ag-Pd	$X_{Pd} = .1-.95$	1000		8
Ag-Sb	$X_{Sb} = .322-.622$	478-648	0.5	41
Ag-Sb	$X_{Sb} = .024-.316$	673-773	0.5	42
Ag-Sn	$X_{Sn} = .3-.9$	900	20.0	9
Ag-Sn	$X_{Sn} = .86-.994$	608-686	20.0	11
Ag-Zn	$X_{Zn} = .28-.82$	773-873	35.0	43
Al-Zn	$X_{Zn} = .05-.9$	560-820	49.5	10
Au-Cd	$X_{Cd} = .56-.99$	520-580	74.0	13
Au-Cd	$X_{Cd} = .16-.76$	640-870	74.0	13
Au-Cu	$X_{Cu} = .42-.78$	620-760	47.0	14
Au-Cu	$X_{Cu} = .15-.85$	120-131	47.0	7
Au-Tl	$X_{Tl} = .8-.9$	723-1023		12
Au-Sn	$X_{Sn} = .22-.9$	773-873	35.0	18
Bi-Cd	$X_{Cd} = .1-.95$	673-873	30.0	19
Bi-Cd	$X_{Cd} = .25-.85$	683-748	30.0	32
Bi-Cd	$X_{Cd} = .164-.857$	695-1123	30.0	20
Bi-Mg	$X_{Mg} = .1-.85$	763-1123	89.0	21
Bi-Pb	$X_{Pb} = .005-.95$	392-743	23.0	22
Bi-Sn	$X_{Sn} = .10-.89$	608	20.5	23

Continued...

Table 2.1 continued.

Bi-Zn	$X_{Zn} = .064-.974$	692-923	35.50	24
Cd-Pb	$X_{Pb} = .063-.89$	648-873	7.0	19
Cd-Pb	$X_{Pb} = .214-.871$	700-845	7.0	20
Cd-Sb	$X_{Sb} = .519-.858$	648-823	30.0	19
Cd-Sb	$X_{Sb} = .104-.6556$	643-788	30.0	26
Cd-Sn	$X_{Sn} = .05-.9$	648-893	9.5	19
Cd-Sn	$X_{Sn} = .15-.75$	773	9.5	32
Cd-Sn	$X_{Sn} = .15-.9$	703-858	9.5	20
Cd-Sn	$X_{Sn} = .18-.92$	633-713	9.5	27
Co-Pt	$X_{Pt} = .27-.68$	970-1181		28
Pb-Sb	$X_{Sb} = .1-.31$	700	23.0	33
Pb-Sb	$X_{Sb} = .13-.84$	643-903	23.0	29
Pb-Sn	$X_{Sn} = .33-.67$	773	0.5	33
Pb-Sn	$X_{Sn} = .91-.99$	683-823	0.5	44
Pb-Zn	$X_{Zn} = .04-.99$	692-923	12.5	24
Pb-Zn	$X_{Zn} = .04-.99$	873	12.5	31
Sb-Sn	$X_{Sn} = .1-.9$	905	20.5	9
Sb-Sn	$X_{Sn} = .86-.92$	685	20.5	17
Sb-Zn	$X_{Zn} = .15-.92$	753-893	25.0	29
Sn-Zn	$X_{Zn} = .14-.85$	704-843	15.0	20

⊕ Values are taken from reference (3).

CHAPTER - III

EQUIPMENT AND PROCEDURE

3.1 Furnace and Temperature Control

A non-inductive nichrome wound tube furnace of 40 ohms resistance was used. The furnace was 60 cms long and 57 mm I.D. The winding was in the middle 35 cms of the furnace tube. 20 cms of the furnace tube was closed at the bottom by a refractory brick. A bottom closed chromium plated nickel tube of 0.5 mm thickness and 20 cms length was placed inside the furnace and earthed to avoid pickup of any induced e.m.f. as well as to homogenise the furnace temperature. A Leeds and Northrup temperature controller was used. A 20 ohms resistance was connected to the relay of the controller such that in the off position about 60 pct. of the current was allowed to pass through the furnace. A 36 gauge chromel-alumel thermocouple was placed between the nickel jacket and the furnace tube and connected to the controller. The cold junction of the thermocouple was placed inside ice-water bath. In this way the temperature of the furnace was controlled to $\pm 2^{\circ}\text{C}$ for a period of 24 hours.

3.2 Design and Fabrication of Cell

The cell was made in a quartz crucible of 45 mm O.D. and 10 cms height. The crucible had a optically flat bottom and two small holes at the top. This crucible rested on quartz beads placed at the bottom of another quartz tube of 50 mm O.D. and 50 cms long. The quartz tube was used so as to be able to evacuate the system at high temperatures. The outside quartz tube had a B-60 high vacuum ground quartz joint attached to the open end. This tube was closed by a B-60 high vacuum ground pyrex joint. The pyrex joint was connected to a closed end 50 mm O.D. pyrex tube. This tube had two side tubes at 180° apart for inlet and outlet of argon gas. The outlet side tube carried a two-way stop cock and extended 20 cms inside the cell as shown in figure 2.1. So as to prevent short circuiting of gas flow. The inlet side was connected to a three way stop cock through a ground glass joint to have connections to the vacuum pump and the gas line. Four tubes of 12 mm diameter were connected on the top of the 50 mm O.D. pyrex tube. Each of these 4 tubes were joined to 6 mm pyrex tubes by using O-ring joints. Figure 2.1 shows the details of the cell. The B-60 joint was prevented from

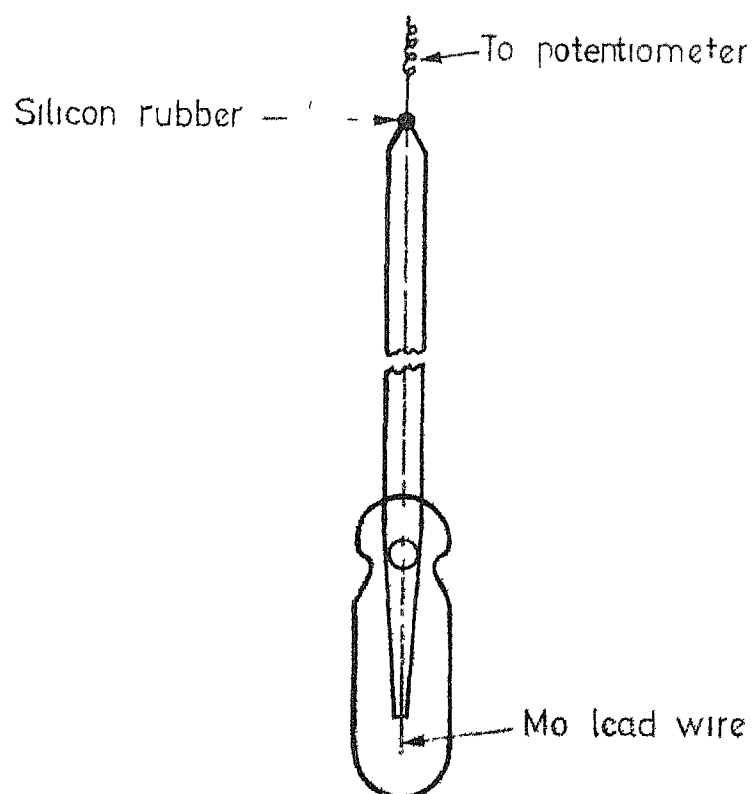


Fig. 3 2 The Electrode

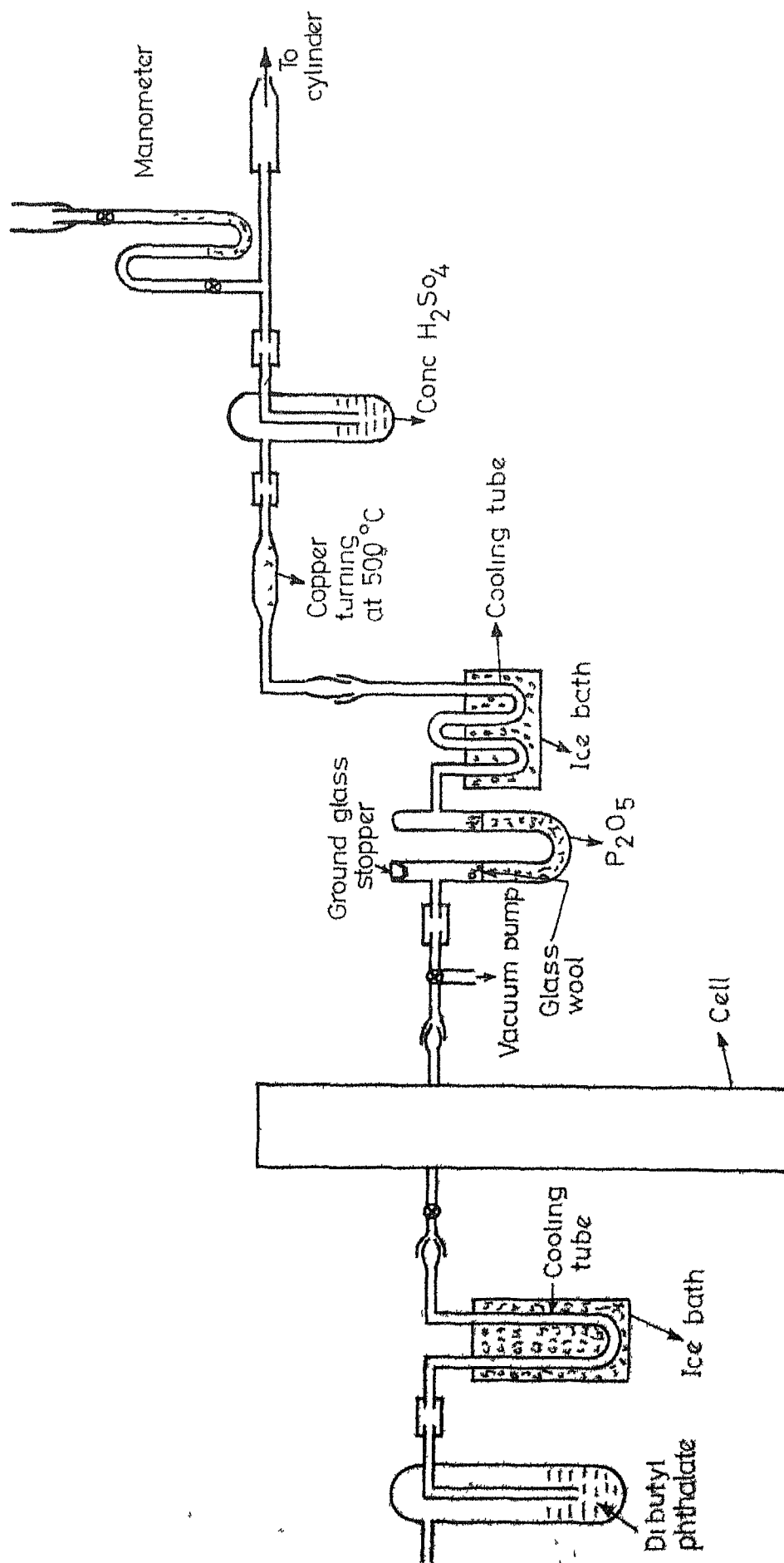


Fig.3.3.3 Gas Purification Train

getting heated up by circulating water through a 6.5 mm diameter Cu tube wound around the joints.

The electrodes as shown in figure 2.2 were made of 6 mm O.D. Vycor tubes of 75 cms length. At one end of this tube was attached another Vycor tube of 2.5 mm diameter and 4 cms length. 1 mm diameter well annealed and **cleaned** molybdenum ^{wires} were sealed inside these tubes. The wire projected about 3 mm at the tip of the 2.5 mm diameter tube. This tip was covered by a bulb of 6 cms length and 9.5 mm O.D. The bulb had 4 holes so that the alloys can be put inside and the electrolyte can get inside the bulb. The other end of the 6 mm Vycor tube was sealed under vacuum with silicon rubber.

3.3 Purification of Gas

The argon used was purified for oxygen and moisture by passing it through concentrated H_2SO_4 , oxygen free copper turning heated to $500^\circ C$ and then passing it through P_2O_5 . The details of the gas purification train is shown in figure 2.3. A U-tube manometer containing dibutyl phthalate was introduced into the system, so as to be able to fill the evacuated cell with argon properly. The gas coming out of the cell was cooled in a U-tube kept in a ice-bath and bubbled out in a bubbler containing dibutyl phthalate.

3.4 Vacuum System

The vacuum system used consists of a diffusion pump backed by a rotary pump of model VS - 4 supplied by Hindhivac Company. The assembly contains a liquid nitrogen trap and a P_2O_5 trap to protect the oil from contamination

3.5 Temperature and E.M.F. Measuring Unit

A type K-4 potentiometer with a d.c. galvanometer manufactured by Leeds and Northrup were used to measure the e.m.f. of the cell. The potentiometer is capable of measuring 0.5 microvolts in the range of 0.16 volts.

The 36 gauge chromel and alumel wires were first annealed by passing a current at 40 volts. The homogeneity of wires was tested by measuring the e.m.f. across a wire when it is pulled through liquid nitrogen. The length of the wire showing constant e.m.f. was selected for making the thermocouple. This wire was twisted and the bead was made by striking arc with a mercury bath kept under kerosene at 40 volts. The hot junction of the thermocouple was passed through a 6 mm diameter Vycor tube closed at the bottom. The thermocouple tube was pushed inside the cell through a O-ring joint at the top of the cell. The cold junction was made by soldering 18 gauge enamelled Cu-wires using a $ZnCl_2$ flux and it was kept in a ice-water bath.

For measuring the e.m.f. of the cell the molybdenum lead wire were connected to 18 gauge enamelled Cu-wires by Cu-connectors. The copper and molybdenum lead wires were covered with polythene sleeves to protect them from draught. These wires were fixed on stands so as to protect them from moving and picking up stray e.m.f.

3.6 Experimental Procedure

3.6.1 Cleaning of the apparatus. The whole glass apparatus was first cleaned by chromic acid care was taken to avoid contact of chromic acid with the ground joints by applying ample amount of grease on the joints. The apparatus was then cleaned with alcohol followed by distilled water. Finally it was cleaned with demineralised water and assembled inside the furnace for drying at 120°C for a period of 24 hours. After drying, the cell was flushed with argon for 2 hours to ensure complete removal of moisture.

3.6.2 Preparation of the electrolyte. The electrolyte was prepared using AR grade of $\text{LiCl}\cdot\text{H}_2\text{O}$, KCl and PbCl_2 of the following purity:

KCl	$\text{LiCl} \cdot \text{H}_2\text{O}$	PbCl_2
Free acid (as HCl) 0.0018	Sulphate 0.04	Pure for analysis
Free alkali (as KOH) 0.0028	As 0.0001	
Al 0.001	Fe 0.002	
As 0.00004	Pb 0.001	
Ba 0.001		
Bromide and Iodide 0.005		
Ca 0.001		
Chlorate 0.003		
Heavy metals (as Pb) 0.0005		
Mg 0.0005		
Phosphate 0.001		
Na 0.02		
Sulphate 0.001		
Nitrogen 0.001		

Since the LiCl-KCl eutectic mixture cannot be effectively dehydrated by vacuum, the salts were dried separately by the following process. Appropriate amounts of $\text{LiCl} \cdot \text{H}_2\text{O}$, KCl and PbCl_2 were weighed to give approximately 104 cc of molten electrolyte. The volume of the molten electrolyte was determined by melting appropriate amounts of the salts in a separate 45 mm diameter pyrex crucible outside the cell. Three tubes of diameter 12 mm^{12 mm} and 18 mm with optically flat bottoms and having holes at the other end

were placed inside the crucible. These tubes were filled with KCl and PbCl_2 . LiCl was put in the crucible. Molybdenum ^{wires} were attached to the holes in the tubes containing KCl and PbCl_2 . The crucible was lowered into the main quartz tube with the help of threads which passed through the holes in the crucible. The main cell was closed, all the O-ring joints were tightened and the vacuum pump was attached to the system.

When evacuation of the cell was started a lot of moisture started coming out. In order to protect the pumps the vacuum system was connected to the cell through a liquid nitrogen trap. The cell was evacuated at room temperature for 24 hours. It was then slowly heated to 40°C and evacuated for 8 hours. The vacuum obtained in this much of time was only 50 microns because of slow process of moisture evolution. The cell was now attached to diffusion pump. With the help of a liquid nitrogen trap the cell was evacuated to 1.5×10^{-6} mm Hg. This vacuum was maintained for about 8 hours. To ensure complete removal of moisture the cell was slowly heated in steps of 5°C to reach 120°C in 6 hours while heating only the backing pump was used. At 120°C the cell was evacuated to 1.5×10^{-6} mm of Hg and maintained for 6 hours. The temperature was increased slowly in steps of 5°C to 150°C in 7 hours. At 150°C the cell was evacuated to 1.5×10^{-6}

mm of Hg for 12 hours to ensure complete removal of moisture. Now the temperature was raised to 500°C at a rate of 25°C per hour while the backing pump was operating. At 500°C the cell was evacuated at 1.5×10^{-6} mm of Hg for 16 hours. Now argon was flushed at 500°C for 15 minutes and the cell was evacuated immediately to 1.5×10^{-6} mm of Hg for 12 hours to remove any moisture carried by argon from rubber tube connections. Now argon was flushed and the temperature was lowered to 400°C . The joint was opened while a torch of argon was kept on the top of the cell. Now the tubes containing KCl and PbCl_2 were taken out with the help of Mo wires allowing the dry KCl and PbCl_2 powder to fall into the crucible containing LiCl. The cell was closed and evacuated. This operation took a few minutes. After evacuation for 2 hours at 1.5×10^{-6} mm of Hg argon was flushed for 15 minutes and the cell was again evacuated for an hour. Argon was introduced into the cell and the temperature was raised to 550°C . A positive pressure was maintained by the flow of argon. The electrolyte was now ready for experimentation

3.6.3 Preparation of electrodes The lead and bismuth used for the preparation of alloys were 99.999 pct. pure. Appropriate amounts of lead and bismuth were weighed on an electronic balance to give 0.1, 0.3, 0.5, 0.7 and 0.9 mole fraction of lead in the alloy. The metals were sealed

under vacuum in a quartz tube and held 150°C above the liquidus temperature for 4 hours. The alloy was taken out by breaking the quartz tube and the process was repeated to ensure homogenisation of the alloy. The alloy was taken out and crushed to a powder of 1 mm particle size, and kept in a dessicator. The tips of molybdenum wires inside the bulbs of electrodes were cleaned by electrolysing in a concentrated NaOH solution⁽¹⁹⁾ at 2 Volt d.c. at 3.5 Amps/cm^2 current density. The molybdenum-wire was the anode and a stainless steel wire was the cathode. The molybdenum tip was then washed with alcohol and dried.

3.6.4 Measurement of e.m.f.: When the electrodes and the electrolyte were ready the outlet stop cock of the cell was closed, the O-ring joints were made loose, the 6 mm blind tubes were taken out and the electrodes were inserted inside the cell chamber. They were kept over the crucible in the temperature range of 500°C . The O-ring joints were tightened and argon flow was stopped. The cell was evacuated for an hour. Argon was introduced into the cell and a positive pressure was maintained inside the cell. The electrodes were slowly rotated and pushed inside the crucible containing electrolyte. The molybdenum lead wires were connected to the potentiometer and the e.m.f readings were taken. It took about 8-12 hours. The temperature was then raised to 575°C and was brought back

550°C. The e.m.f. was noted again as a function of time until it was constant. It took about a couple of hours. Now the temperature was lowered to 525°C and was again brought back to 550°C. The e.m.f. was noted again until it was constant, ~~again~~. The values of the e.m.f. reported in Chapter - IV are the average e.m.f. values of the three e.m.f. readings. When the e.m.f. readings were taken the temperature of the cell was read simultaneously with the help of another potentiometer.

IIT KANPUR
CENTRAL LIBRARY
Acc. No. A45522

CHAPTER - IV

RESULTS

4.1 The Partial Molar Free Energy and the Activity of Lead

From the observed values of e.m.f. the partial molar free energies, $\Delta \bar{G}_{Pb}$, for the different mole fraction of lead i.e. $X_{Pb} = 0.1 - 0.9$ can be obtained directly from the equation,

$$\Delta \bar{G}_{Pb, X_{Pb}} = - nFE$$

where

$n = 2$ (since the valence change occurring $Pb \rightarrow Pb^{++}$ is 2)

F = Faraday constant 23061 cal/volt equivalent

E = The measured e.m.f. in volts

These $\Delta \bar{G}_{Pb}$ values are recorded in Table 4.1. The activities of Pb in liquid alloys can be obtained from the following equation,

$$\Delta \bar{G}_{Pb, X_{Pb}} = RT \ln a_{Pb} \quad (4.1)$$

These values of a_{Pb} are also listed in the same Table 4.1.

4.2 Partial Molar Free Energies of the Component in the Pb-Bi Alloys

With the help of excess partial molar properties we can proceed with the further calculations. These excess quantities are identified below by the superscript 'ex'. The excess partial molar free energies of lead can be calculated by the following equation,

$$\Delta \bar{G}_{\text{Pb}, X_{\text{Pb}}}^{\text{ex}} = \Delta \bar{G}_{\text{Pb}} - \Delta \bar{G}_{\text{Pb}}^{\text{id}} \quad (4.2)$$

where

$$\Delta \bar{G}_{\text{Pb}}^{\text{id}} = RT \ln X_{\text{Pb}}$$

These excess free energies of formation of lead are calculated by taking $\Delta \bar{G}_{\text{Pb}}$ values from eq. 4.1.

The corresponding excess partial molar free energies of Bi are calculated by graphical integration of the Gibb's-Duhem eqn. of the following form⁽³⁾

$$\Delta \bar{G}_{\text{Bi}, X_{\text{Bi}}}^{\text{ex}} = - \alpha_{\text{Pb}} X_{\text{Pb}} X_{\text{Bi}} - \int_{X_{\text{Bi}}=1}^{X_{\text{Bi}}} \alpha_{\text{Pb}} dX_{\text{Bi}} \quad (4.3)$$

where

$$\alpha_{\text{Pb}} = \frac{\Delta \bar{G}_{\text{Pb}}^{\text{ex}}}{(1 - X_{\text{Pb}})^2}$$

These α_{Pb} values calculated from the experimental data at $X_{Pb} = 0.1, 0.3, 0.5, 0.7$ and 0.9 were plotted as a function of composition. The values of α_{Pb} corresponding to data $X_{Pb} = 0.2, 0.4, 0.6$ and 0.8 were obtained from the same plot. From the areas obtained by Simpson's rule for each composition of Pb (i.e. $X_{Pb} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9) the $\Delta \bar{G}_{Bi, X_{Bi}}^{ex}$ values are calculated.

These partial molar quantities at $823^\circ K$ for the lead component and bismuth component in the liquid Pb-Bi alloys are listed in Tables 4.2 and 4.3 respectively.

\bar{G}_{Pb} and $\Delta \bar{G}_{Bi}$ values for different composition are calculated from eq. (4.2). These values are also listed in Table 4.2 and 4.3. The activities of the components are calculated by eq. (4.1) and the corresponding activity coefficient, γ were calculated by formula $\gamma = a/X$. These activities and activity coefficients are listed in Tables 4.2 and 4.3.

The partial molar free energies are plotted in figure 4.1 and the partial molar excess free energies are plotted in figure 4.2. The activities and activity coefficients are plotted in figure 4.3. All the figures show expected and consistent behaviour of the alloys.

4.3 Integral Molar Properties

These values are obtained from the partial molar properties of lead and bismuth components by the following equations,

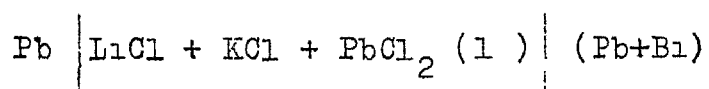
$$\Delta G = X_{Pb} \Delta \bar{G}_{Pb} + X_{Bi} \Delta \bar{G}_{Bi} \quad (4.4)$$

$$\text{and} \quad -G^{ex} = X_{Pb} \Delta \bar{G}_{Pb}^{ex} + X_{Bi} \Delta \bar{G}_{Bi}^{ex} \quad (4.5)$$

The values of ΔG and $-G^{ex}$ obtained for different compositions are listed in Table 4.4. These values are also plotted in figure 4.1 and 4.2 showing consistent behaviours.

The ΔH values calculated from the $\frac{dE}{dT}$ values obtained from data of e.m.f. measurements are not reliable^(22,33,40). Kleppa's⁽⁴⁵⁾ as reported values of ΔH at 623°K and 723°K. His data shows that ΔC_p for these alloys is zero i.e. H is independent of temperature. Therefore his data at 723°K are taken for further calculations. From this ΔH and our ΔG values, ΔS values are calculated and listed in Table 4.4. The ΔS and $-S^{ex}$ values are plotted in figure 4.4 along with the values of ΔS^{ld} . It may be noted that the S^{ex} values varies in a different way from the previous workers.

Table 4.1 E.m.f. obtained with the cell



at 823°K

Composition of the alloy X_{Pb}	E.m.f. (Volts)	$\Delta \bar{G}_{\text{Pb}}$ cal/mole	a_{Pb}
0.1	0.112,000 \pm 0.00050	-5165	0.045
0.3	0.050,820 \pm 0.00025	-2340	0.235
0.5	0.030,500 \pm 0.00010	-1405	0.425
0.7	0.015,850 \pm 0.000050	-730	0.640
0.9	0.003,550 \pm 0.000003	-165	0.900

Table 4.2 Partial molar quantities for liquid Pb-Bi alloys at 823°K (Pb component)

x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta \bar{G}_{\text{Pb}}$ cal/mole	$\Delta \bar{G}_{\text{Pb}}^{\text{ex}}$ cal/mole
0.0	0.000	(0.120)	($-\infty$)	(-2320)
0.1	0.045	0.450	-5165	-1400
0.2	0.125	0.630	-3340	-710
0.3	0.235	0.780	-2340	-370
0.4	0.330	0.825	-1795	-295
0.5	0.425	0.850	-1405	-270
0.6	0.525	0.870	-1065	-230
0.7	0.640	0.915	-730	-145
0.8	0.775	0.970	-415	-50
0.9	0.900	1.000	-165	+7
1.0	1.000	1.000	0	0

Table 4.5 Partial molar quantities for liquid Pb-Bi alloys at 823°K (Bi component)

X_{Bi}	a_{Bi}	γ_{Bi}	$\Delta \bar{G}_{Bi}^{ex}$ cal/molc	$\Delta \bar{G}_{Bi}'$ cal/mole
1.0	1.000	1.00	0	0
0.9	0.875	0.97	-50	-220
0.8	0.725	0.91	-170	-535
0.7	0.600	0.86	-275	-855
0.6	0.500	0.84	-310	-1145
0.5	0.410	0.82	-330	-1465
0.4	0.315	0.79	380	-1880
0.3	0.215	0.72	-540	-2510
0.2	0.115	0.57	-930	-3560
0.1	0.050	0.50	-1155	-4920
0.0	0.000	(0.13)	- ∞	(-1170)

Table 4.4 Integral quantities for liquid Pb-Bi alloys at 823°K

X_{Pb}	X_{Bi}	ΔH^\ominus cal/mole	ΔG cal/mole	ΔS cal/mole-deg	ΔG^{ex} cal/mole	ΔS^{ex} cal/mole-deg
0.1	0.9	-80	-715	0.772	-185	0.12
0.2	0.8	-155	-1095	1.142	-280	0.14
0.3	0.7	-210	-1300	1.324	-305	0.11
0.4	0.6	-245	-1400	1.403	-305	0.06
0.5	0.5	-250	-1435	1.440	-300	0.06
0.6	0.4	-235	-1390	1.403	-290	0.07
0.7	0.3	-205	-1265	1.288	-265	0.07
0.8	0.2	-150	-1045	1.088	-225	0.09
0.9	0.1	-80	-640	0.680	-110	0.03

[⊕] Values taken from reference (45).

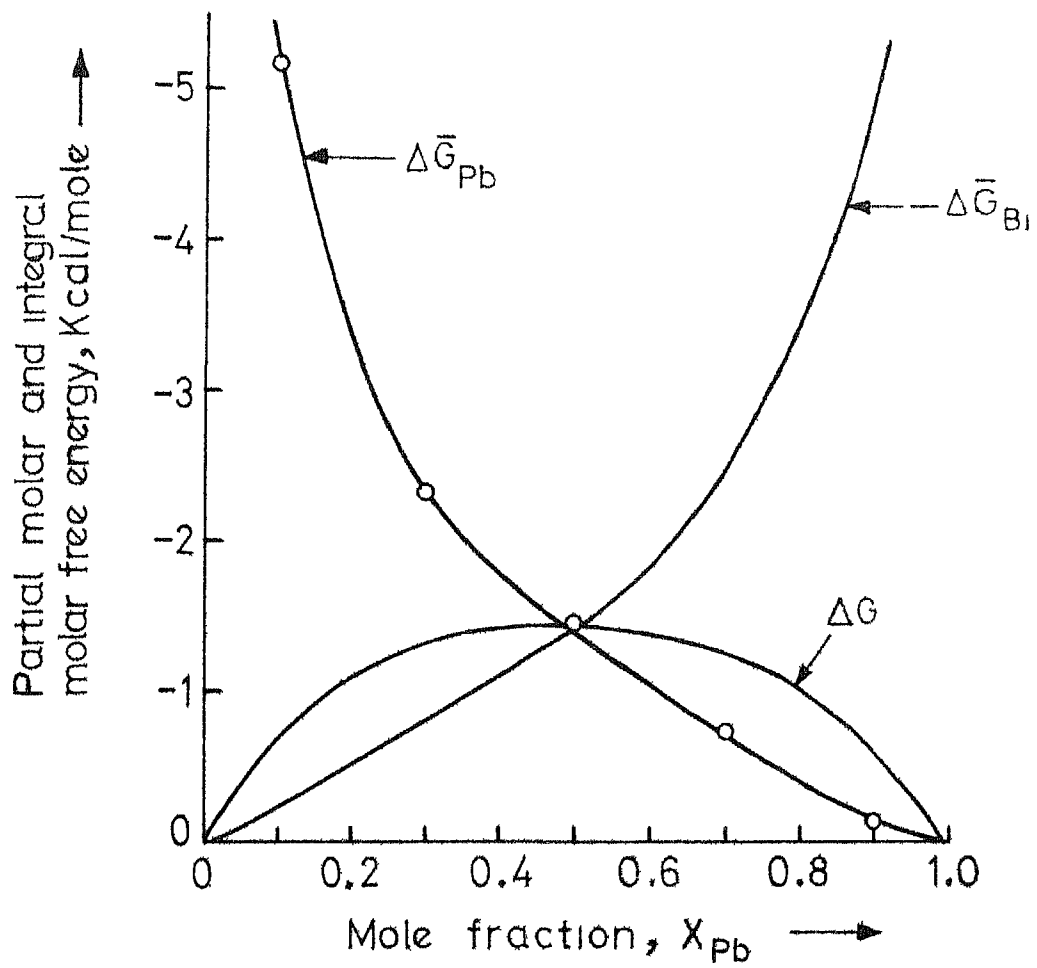


Fig 4.1 Partial molar and integral molar free energies of the Pb-Bi alloys at 823°K

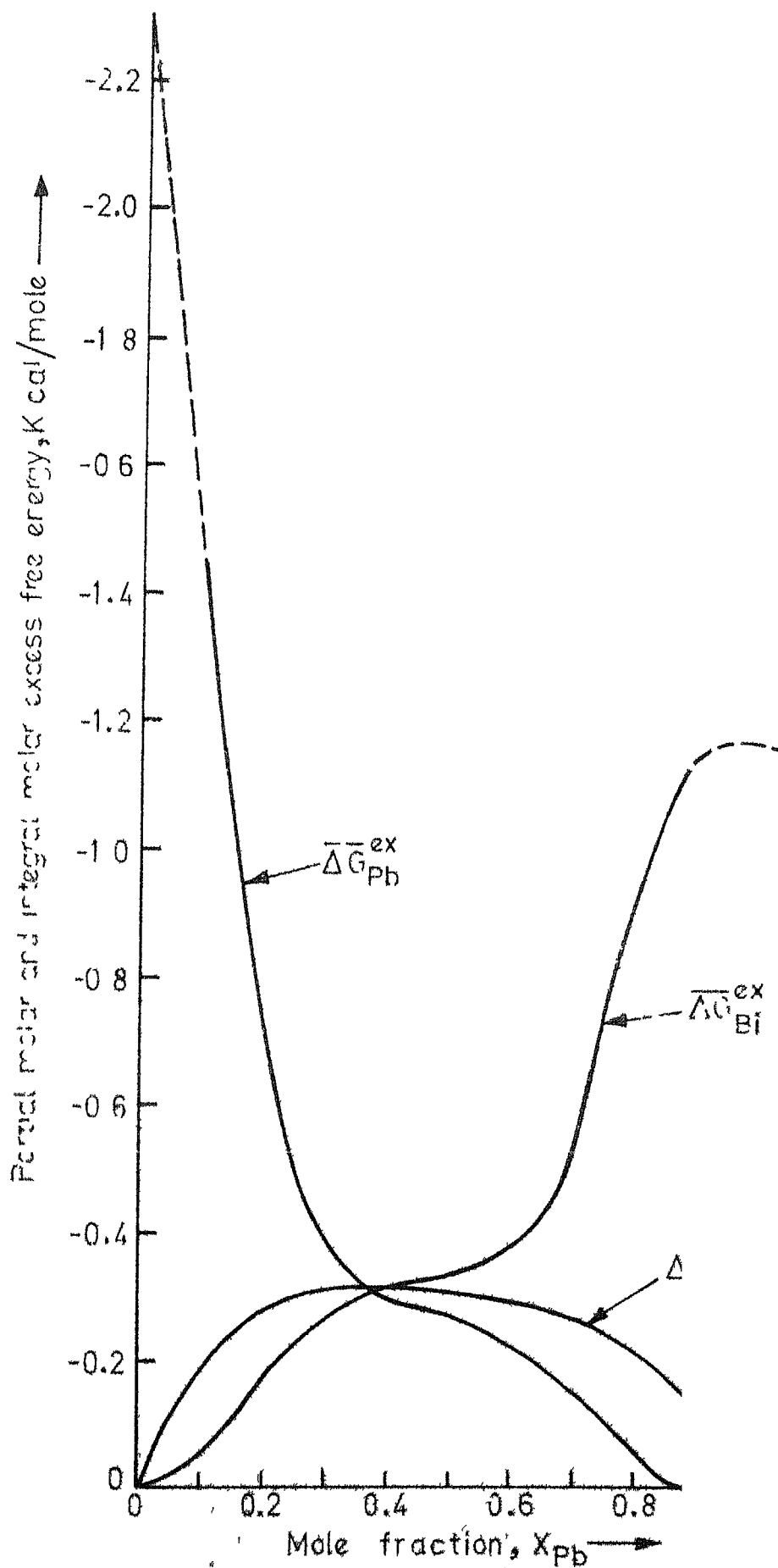


Fig.4.2 The partial molar and integral molar excess free energies of the Pb-Bi alloys at 823°K

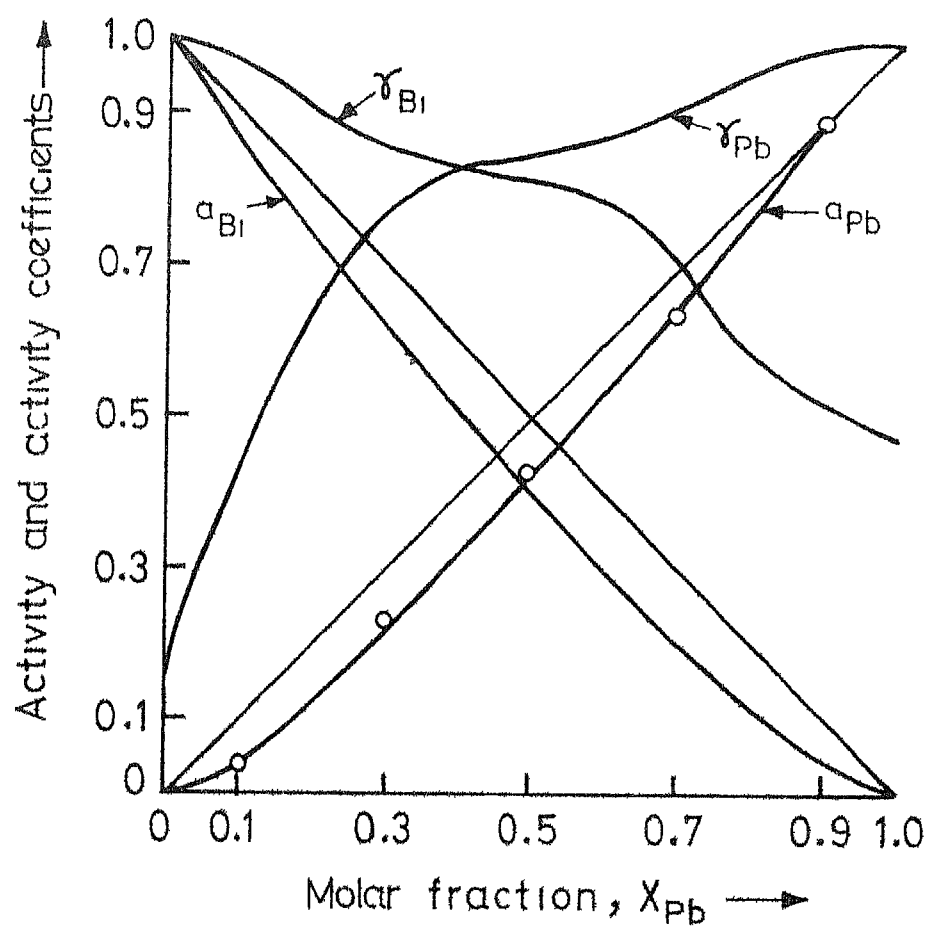


Fig.4.3 Activity and activity coefficients of the components in the Pb-Bi alloys at 823 °K

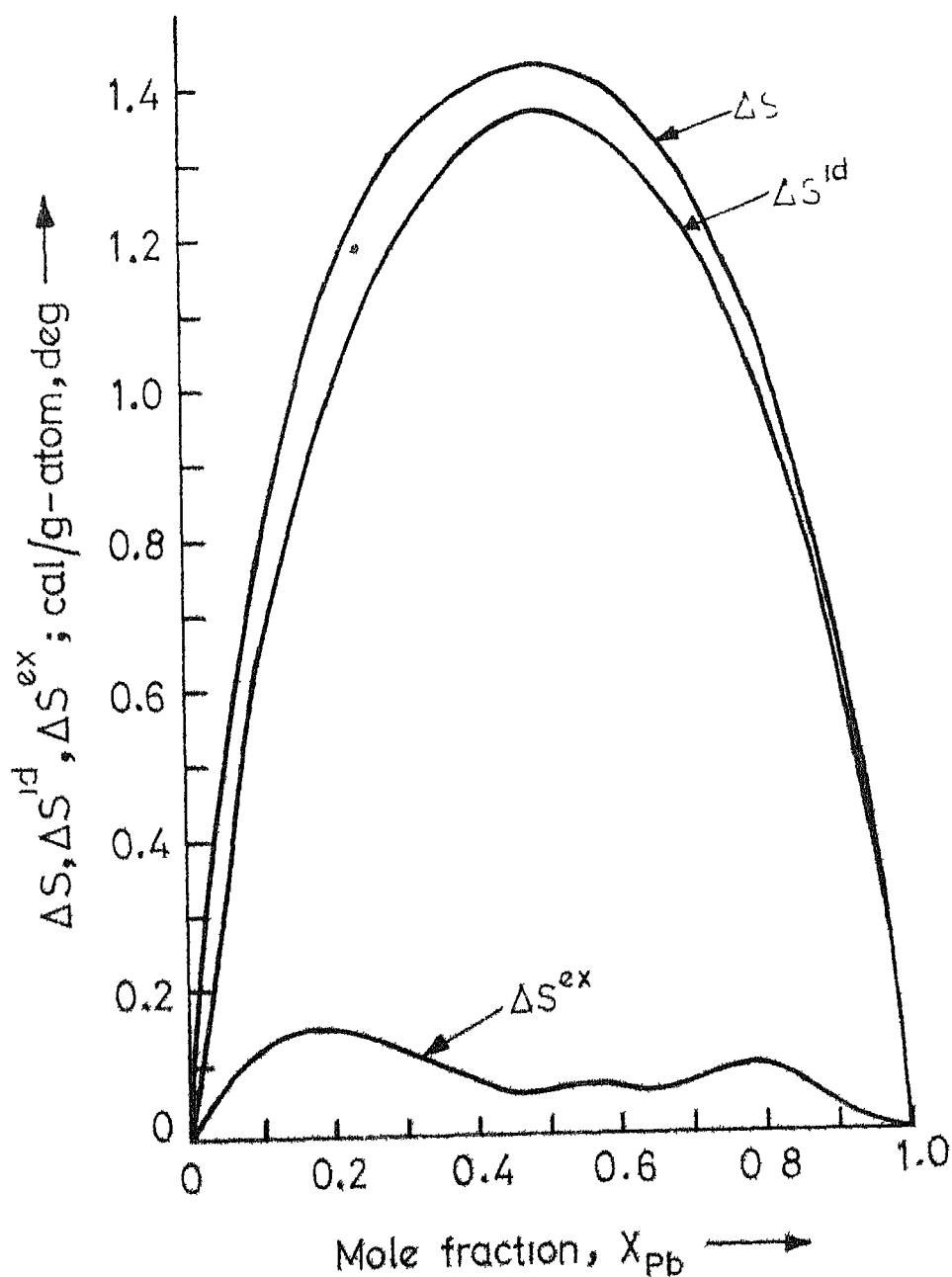


Fig. 4.4 Entropy of formation, ideal entropy of formation and excess entropy of formation of Pb-Bi alloys at 823°K.

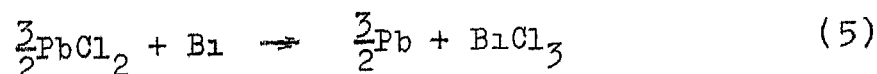
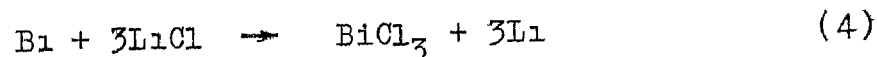
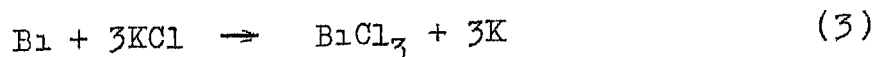
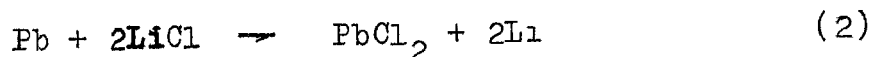
CHAPTER - V

DISCUSSIONS

5.1 Sources of Errors

The various sources of errors which can occur in the e.m.f. measurements are discussed below.

Side reactions During the measurements secondary reactions i.e. reactions other than the cell reactions can give rise to errors. The following are the side reactions which may occur during the measurements



The activities of Li, K, and BiCl_3 are calculated on the basis of the standard free energies of formation of chlorides^(2,3) and assuming equilibrium in all the above cases. Those values are tabulated below

Reaction	Activities
1	$a_K \approx 10^{-27}$
2	$a_{Li} \approx 10^{-23}$
3	$a_{BiCl_3} \approx 10^{-71}$
4	$a_{Li} \approx 10^{-70}$
5	$a_{BiCl_3} \approx 10^{-14}$

These values are much smaller compared with the values calculated for the cells used in the literature. Therefore the side reactions are assumed to be negligible. From the activity of $BiCl_3$ it can be seen that the amount of bismuth going into the molten electrolyte is negligible. So the alloy electrode composition remains constant before and after the experiments. Also the diffusion in liquid alloys is generally very high and the diffusion coefficient is of the order of 10^{-8} cm/sec. So any small gradation in the liquid electrode will tend to homogenise rapidly.

The side reactions due to the impurities have been avoided. To avoid dust the whole system was thoroughly cleaned before use. The molybdenum lead wires had an oxidised surface. To remove it these were electrolysed to clean the surface. To make sure that the gas train does not introduce any impurities, the argon was purified and flushed through the gas train for 15 minutes, before

passing it through the main cell. To avoid side reactions due to moisture and volatile matter present in the electrolyte prolonged evacuation and heating as discussed in Chapter - III were carried out. Sufficient amount of PbCl_2 (1 mol. wt /) was added to avoid reduction of PbCl_2 by baser metals.

Stray e.m.f.: The stray e.m.f. produced by the furnace windings were reduced by chrome-plated earthed nickel sheet. The furnace was switched off for a second while the e.m.f. was being measured. This did not alter the cell e.m.f., confirming that there was no pick up of e.m.f. from the furnace windings. The contact potentials in the measuring units were reduced by using copper single strand wires. Any induced e.m.f. pick up by the measuring units were reduced by the copper earthed mesh over the copper lead wires. The contacts of the lead wires were kept clean and free from air circulation to avoid any e.m.f. pick up. Thus the stray e.m.f. which may alter the cell e.m.f. was avoided.

Reversibility of the cell The reversibility of the cell was confirmed by the following manner. The furnace temperature was raised to a higher value and then the system was brought back to original temperature. The e.m.f. at this temperature was measured. Again disturbing

the system to lower temperatures and bringing it back to original temperature the e.m.f. was measured. Values of e.m.f. were found to be consistent at the temperature of measurement. The temperature was controlled to $\pm 1^\circ\text{C}$ during the measurements. On the basis of available partial molar enthalpies⁽⁴⁸⁾ it is found that at this temperature variation of $\pm 1^\circ\text{C}$ would have negligible effect on the e.m.f.

Ionic conduction. The cell must not have any electronic conduction. This arises at higher temperatures and from emulsion of metals in electrolyte and impurities. Precautions have been taken to minimise this. Also the system itself has very low vapour pressure which will prevent evaporation of metals.⁽⁴⁶⁾ Evaporation generally leads to change of composition as well as electronic conduction.

5.2 Comparison With Other Data

The values of the $\Delta\bar{G}_{\text{Pb}}$ obtain in present work (Table 4.1) are consistent with the $\Delta\bar{G}_{\text{Pb}}$ values obtained by previous investigators^(22,33,47). The $\Delta\bar{G}_{\text{Pb}}$ values of lead reported by Strickler et al⁽²²⁾ and Elliott et al⁽³³⁾ are plotted in figure 5.1 along with those obtained by this study. This figure shows that both sets of data are close to the present results. The data of

Elliott et al⁽³³⁾ at 773°K are less negative than those reported in this investigation at 823°K. The results of Strickler et al⁽²²⁾ corresponding to 700°K are also less negative. Thus the present results compare well with other data.

5.3 Internal Consistency of the Results

The internal consistency of the present results is confirmed by the following

- 1) From figure 4.1 it is observed that a_{Pb} , $-\bar{G}_{Pb}$, a_{Bi} and $\Delta\bar{G}_{Bi}$ show smooth regular behaviour with composition
- 2) The $\Delta\bar{G}_{Pb, X_{Pb}}$, $\Delta\bar{G}_{Bi, X_{Bi}}$ values obtained by the same cell at 848°K⁽⁴⁹⁾ were more negative than those obtained at 823°K.
- 3) The values of $\Delta\bar{G}_{Pb}$ at 823°K calculated with the available $\Delta H^{(45)}$ values and $\Delta\bar{G}_{Pb}$ at 848°K⁽⁴⁹⁾ were in good agreement with those obtained experimentally at 823°K.

5.4 The Bonding in the Pb-Bi Alloys

The entropy of formation ΔS is found to be more than the ideal entropy. This suggests that there are contributions other than the configurational entropy

which makes ΔS greater than ΔS^{ld} . These contributions may be from vibrational entropy, as other contributions to ΔS of the Pb-Bi alloy are expected to be negligible. This excess entropy against composition curve shows two minimas at $X_{Pb} = 0.45$ and $X_{Pb} = 0.65$. At these compositions the positive contribution to ΔS appears to be less. This can arise either because of clustering or segregation. Around the composition $X_{Pb} = 0.45$ the Pb-Bi phase diagram (fig. 5 2) shows a eutectic, which suggests that segregation in the liquid alloy at this composition may have been present. The phase diagram also shows a compound at about $X_{Pb} = 0.68$. This again suggests association in the liquid state. It is thus postulated that in the Pb-Bi alloys the bonding is weaker which makes the ΔS more positive than ΔS^{ld} and also there is association in the liquid state around $X_{Pb} = 0.65$ and segregation in the liquid state also around $X_{Pb} = 0.45$. This view is consistent with the experimental ΔS^{ex} values and the phase diagram.

It may be noted that ΔS^{ex} values obtained from the average free energy values^(22,40) of the previous workers and the calorimetric heats of formation of Fleppa⁽⁴⁵⁾ do not seem to be consistent with the phase diagram.

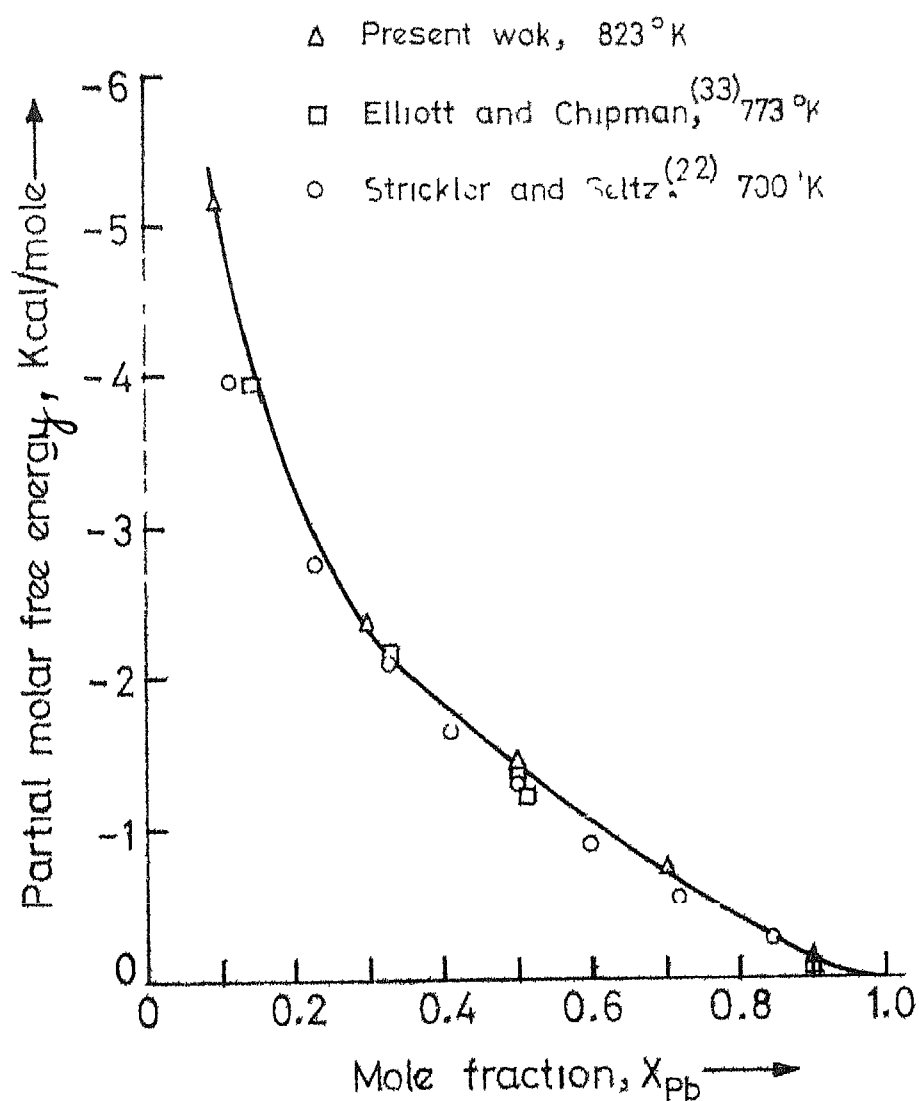


Fig. 5.1 Experimental values of the partial molar free energies of lead in the liquid Pb-Bi alloys

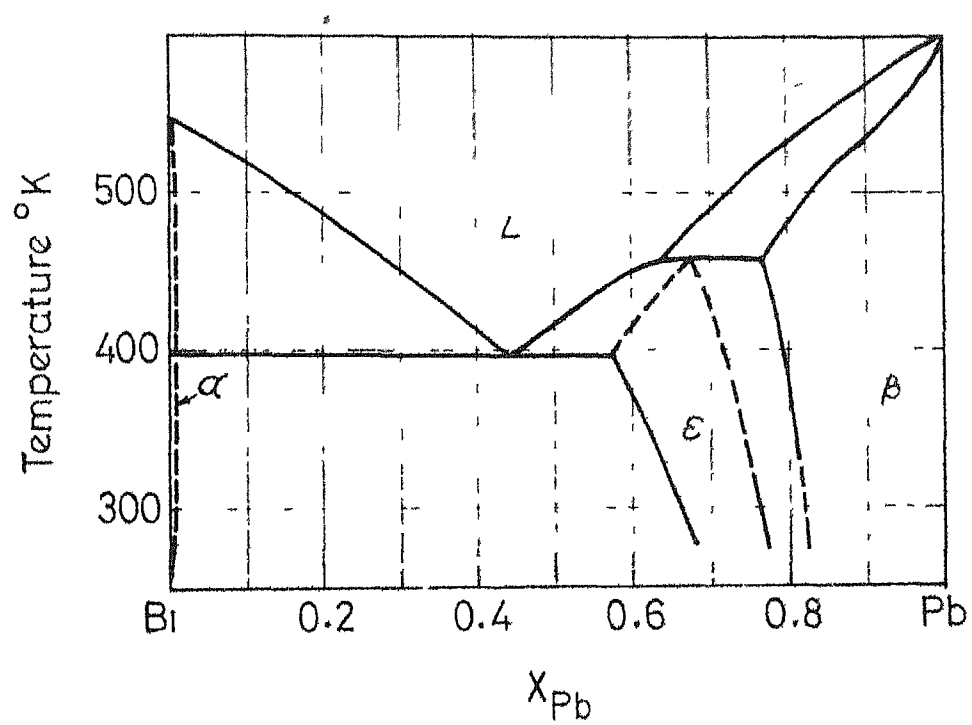


Fig. 5.2 Bismuth lead system

CHAPTER - VI

SUMMARY AND CONCLUSIONS

1. Activity of lead in lead-bismuth alloys 823°K are measured at $X_{Pb} = 0.1, 0.3, 0.5, 0.7$ and 0.9 in the galvanic cell $Pb \mid LiCl + KCl + PbCl_2 \mid (Pb+B_1)$.
2. Activities and activity coefficients of lead and bismuth and $\Delta \bar{G}_{Pb}$, $\Delta \bar{G}_{Bi}$, $\Delta \bar{G}_{Pb}^{ex}$ and $\Delta \bar{G}_{Bi}^{ex}$ values at 823°K are calculated, tabulated at $X_{Pb} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 .
3. ΔG^{ox} and ΔG values for all compositions are tabulated.
4. By taking the calorimetric values⁽⁴⁵⁾ ΔS and ΔS^{ex} values are calculated.
5. All these thermodynamic functions are internally consistent, and consistent with other published data.
6. The variation of ΔS^{ex} with composition suggests that in the liquid alloy there is segregation at about $X_{Pb} = 0.45$ and association at about $X_{Pb} = 0.65$.

REFERENCES

1. Techniques of metal research, Vol. IV, Part I,
R.A. Rapp (Ed.), Interscience Publishers, New
York (1970)
2. O. Kubaschewski and E.L.L. Evans, Metallurgical
Thermochemistry, International Series of Monographs on
Metal Physics and Physical Metallurgy, Pergamon Press Ltd,
London (1958)
3. R.W. Gurry and L.S. Darken, Physical Chemistry of
Metals, Mc Graw-Hill Book Company, Inc, New York (1953)
4. C. Wagner and A. Werner, J. Electrochem Soc. 110, 326
(1963)
5. A. Olander, J. Am. Chem. Soc. 53, 3577, (1931)
6. A. Watcher, J. Am. Chem. Soc. 54, 4609, (1932)
7. R.A. Oriani, Acta Met. 4, 15 (1956)
8. J.N. Pratt, Trans. Faraday Soc. 56, 975 (1960)
9. R.O. Frantik and H.J. McDonald, Trans. Electrochem.
Soc. 88, 253 (1945)
10. B.L. Averbach, M. Hillert and M. Cohen, Acta Met. 2,
621 (1954)
11. Thomas C. Wilder, Trans. AIME 233, 1202 (1965)
12. O.J. Kleppa, J. Am. Chem. Soc. 73, 385 (1951)
13. A. Olander, J. Am. Chem. Soc. 54, 3819 (1932)
14. R.A. Oriani, Acta Met. 2, 608 (1954)
15. L.L. Seigle, J. Metals 8, 91 (1956)
16. O.J. Kleppa, J. Am. Chem. Soc. 71, 3275 (1949)

17. J.A. Yanko, A.E. Drake and F. Hovorka, Trans. Electrochem. Soc. 89, 357 (1946)
18. O.J. Kleppa, J. Am. Chem. Soc. 72, 3346 (1950)
19. J.F. Elliott and J. Chipman, Trans. Faraday Soc 47, 138 (1951)
20. N.W. Taylor, J. Am. Chem. Soc. 45, 2865 (1923)
21. J.T. Egan, Acta Met. 71, 560 (1959)
22. H.S. Strickler and H. Seltz, J. Am. Chem. Soc. 58, 2084 (1936)
23. H. Seltz and F.J. Dunkerley, J. Am. Chem. Soc 64, 1392 (1942)
24. O.J. Kleppa, J. Am. Chem. Soc. 74, 6052 (1952)
25. T.A. Trunbore, W.E. Wallace and R.S. Gaig, J. Am. Chem. Soc. 74, 132 (1952)
26. H. Seltz and B.I. Dewitt, J. Am. Chem. Soc 60, 1305 (1938)
27. J.H. McAteel and H. Seltz, J. Am. Chem Soc. 58, 2081 (1936)
28. R.A. Ollani, Acta Met. 1, 144 (1953)
29. H. Seltz and Bernard J. Dewitt, J. Am. Chem. Soc. 61, 2594 (1939)
30. J.H. Hildebrand and J.N. Sharma, J. Am. Chem. Soc. 51, 462 (1929)
31. F.D. Rosenthal, G.J. Mills and F.J. Dunkerley, Trans. Met. Soc. AIME 212, 153 (1958)

32. S. Mellgren, J. Am. Chem. Soc. 74, 5037 (1952)
33. J.F. Elliott and J. Chipman, J. Am. Chem. Soc. 73, 2682 (1951)
34. J. Wagner and A. Werner, J. Electrochem. Soc. 110, 326 (1963)
35. H.A. Latinen, W.S. Ferguson and R. A. Osteryoung, J. Electrochem. Soc. 104, 516 (1957)
36. H.J. Gardner, C.T. Brown and G.J. Janz, J. Phy. Chem. 60, 1458 (1956)
37. C. Solomans, J. Goodkin, H.J. Gardner and G.J. Janz, J. Phy. Chem. 62, 248 (1958)
38. Betts, Lead refining by electrolysis, John Wiley and Sons, Inc., New York (1908)
39. E.H. Swift, J. Am. Chem. Soc. 45, 371 (1923)
40. C. Wagner and G. Engelhardt, Z. Physik Chem 159, 241 (1932)
41. A.G. Vorduch and C. Wagner, J. Phys. Chem. 61, 558 (1957)
42. F. Weibke and I. Efesiger, Z. Elektrochem. 46, 61 (1940)
43. W. Trzebiatowski and J. Terpilowske, Bull. Acad. Polon. Sci., 3, 391 (1955)
44. R.A. Schaefer and F. Hovorka, Electrochem. Soc. Reprint No. 87, 23, 267 (1945)

45. O.J. Kloppe, J. Phy. Chem. 59, 354 (1955)
46. O. Kubaschewski and F.E. Wittig, Z. Electrochem. 47, 433 (1941)
47. V. Valenti, L. Obari and H. Fiorari, Gazz. Chim. ital, 84, 11 (1956)
48. R. Hultgren, R.L. Orr, P.D. Anderson and K.K. Kelley, Selected values of thermodynamic properties of metals and alloys, John Wiley & Sons Inc, New York (1963)
49. R.C. Agarwala, 'A Thermodynamic Investigation of the Liquid Pb-Bi Alloy at 848°K', M.Tech thesis, I.I.T. Kanpur (1975)

A 45522

No.
669.9

A 45522
Date Slip

D 26t This book is to be returned on the
date last stamped

CD 6729

ME- 1975-M-DAS- THE